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SYNTHESIS OF ELASTOMERS CONTAINING Si-N BONDS IN
THE MAIN CHAIN

QUARTERLY PROGRESS REPORT NO. 6
1 January - 31 March 1963

Contract No. DA-23-072-ORD-1687
Dept. of Army Project No. 593-32-002

M.R.I. Project No. 2531-C

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For

Rock Island Arsenal
Rock Island, Illinois

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THE MAIN CHAIN**

by

L. W. Breed
R. L. Elliott

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PREFACE

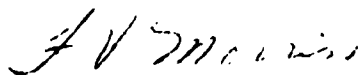
This report was prepared by Midwest Research Institute under U. S. Army Contract No. DA-23-072-ORD-1687. The work was administered under the direction of Rock Island Arsenal, Rock Island, Illinois, with Mr. Z. T. Ossefort acting as Project Officer.

This report covers work conducted from 1 January - 31 March 1963.

Project personnel were Messrs. Richard Elliott and L. W. Breed, who acted as project leader.

Approved for:

MIDWEST RESEARCH INSTITUTE



F. V. Morriss, Director
Chemistry Division

15 April 1963

ABSTRACT

Improvement in the hydrolytic stability of polymers prepared by the condensation of silazanes with organic diols is observed when N-H groups in the polymer chain are replaced by N-methyl groups. Several new diols have been examined in this type of polymerization, but none of the materials equal resorcinol, 1,4-benzenedimethanol, 4,4'-dihydroxybiphenyl, or bisphenol "A". In studies of the reactions of cyclic silicon-nitrogen compounds under the influence of acidic or basic catalysts at 175°, it was concluded that the chief reaction involves randomization of the cyclic structure. A new polymer containing phenylene groups and silicon and nitrogen in the main chain is reported.

TABLE OF CONTENTS

	<u>Page No.</u>
I. Introduction	1
II. Discussion	1
A. Polymers from Silazanes and Organic Diols	1
B. Reactions of Cyclic Silazanes Under the Influence of Acids and Bases	4
C. Silicon-Nitrogen Polymer Containing Phenylene Groups . . .	4
D. Other Experiments	5
III. Future Work	5
Experimental Part	6
A. Hydrolytic Stability of Silicon-Nitrogen Compounds and Polymers.	6
B. Polymers from Silazanes with Organic Diols	11
C. Rearrangement Reactions of Cyclosilazanes	16
D. Phenylene-Linked Silazane Polymers	17
E. Miscellaneous Experiments	18
Bibliography	20
Appendix	21

I. INTRODUCTION

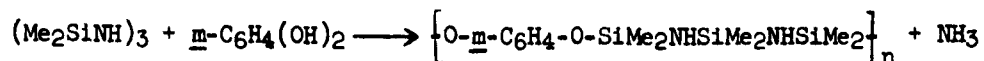
The objective of the work described in this report is the synthesis of thermally and hydrolytically stable elastomers based on main chains consisting predominantly of silicon atoms bonded directly to nitrogen atoms. In earlier reports of work under this contract, attention has centered on a search for methods of preparing high molecular weight, linear silicon-nitrogen polymers.

Two satisfactory polymerization procedures have been found. In one method, 1,3-bis(aminodimethylsilyl)-2,2-dimethyl-1,3-diaza-2-silacyclopentane and related compounds, heated in the presence of a catalyst, give polymers with intrinsic viscosities up to 0.2. By a second procedure, condensation reactions of organic diols with cyclic silazanes yield polymers with intrinsic viscosities as high as 1.6, the molecular weight depending on the identity of the reactants. Other approaches to the preparation of silicon-nitrogen polymers have been investigated, for example rearrangements of cyclic silazanes in the presence of catalysts, but suitable materials for elastomeric compositions have not been obtained.

II. DISCUSSION

A. Polymers from Silazanes and Organic Diols

The condensation of silazanes with organic diols has been discussed in detail in Quarterly Progress Reports Nos. 4 and 5. Typical of this method of polymerization is the reaction of hexamethylcyclotrisilazane and resorcinol, which can be represented as follows:



In screening reactions, which employed hexamethylcyclotrisilazane as the silazane, resorcinol, 1,4-benzenedimethanol, bisphenol "A", or p,p'-dihydroxybiphenyl yielded polymers with the most promising properties. The use of other silazanes has not been investigated intensively, but materials with reasonable degrees of polymerization have been obtained from nonamethylcyclotrisilazane and 1,3-bis(methylamino)pentamethyldisilazane as well as from hexamethylcyclotrisilazane.

1. Screening of new monomers: During this report period, several different diols were examined and found to have no particular advantage over those investigated earlier. The new diols include 2,2,4,4-tetramethyl-1,3-cyclobutanediol, 4,4'-oxydiphenol, and 4,4'-bis(hydroxymethyldiphenyl)ether. N-trimethylsilylhexamethylcyclotrisilazane was used as the silazane in one reaction with bisphenol "A", but a high polymer was not obtained.

2. Hydrolytic stability: In order to assess the effect of monomeric composition on the hydrolytic stability of polymers, it was necessary to develop a procedure capable of determining the relative stability of polymers against hydrolysis under controlled conditions. Of the methods described in the literature for following the reaction rates of systems containing silazanes or silylamines, the procedure used by Pike¹ for determining the kinetics of the reaction between silazanes and silanols appeared to be the most attractive. In this procedure, ammonia formed in the reaction is swept from the system with nitrogen and absorbed in a boric acid solution which is later titrated with dilute hydrochloric acid.

It was found that Pike's procedure could be successfully applied to differentiate the relative rates of reaction of monomeric silazanes with water. However, ammonia evolution was too slow to provide the needed differentiation within a reasonable length of time when polymers were hydrolyzed under these conditions. Also, because several hours were required to dissolve polymers in the solvent, difficulties in maintaining anhydrous solutions introduced erratic results. Higher reaction temperatures failed to increase the reaction rate sufficiently to give the needed differentiation between hydrolytic stabilities.

It was found that these difficulties could be overcome if mixtures of toluene and wet methanol were used as the solvent for the hydrolysis. The solutions were heated at 65° and the evolved ammonia was collected and determined in the manner described previously. The results of applying this procedure to a series of polymers are summarized in Figs. 1, 2, and 3.

Of particular interest is the marked increase in hydrolytic stability, both in monomers and polymers, when the N-H group is replaced by the N-methyl group. The curves in Fig. 1 reflect the increase in hydrolytic stability achieved in substituted monomeric derivatives of hexamethylcyclotrisilazane. Little difference can be observed in Figs. 2 and 3 when various diols are used in polymer preparation, but the hydrolytic stability is substantially increased when nonamethylcyclotrisilazane is substituted for hexamethylcyclotrisilazane.

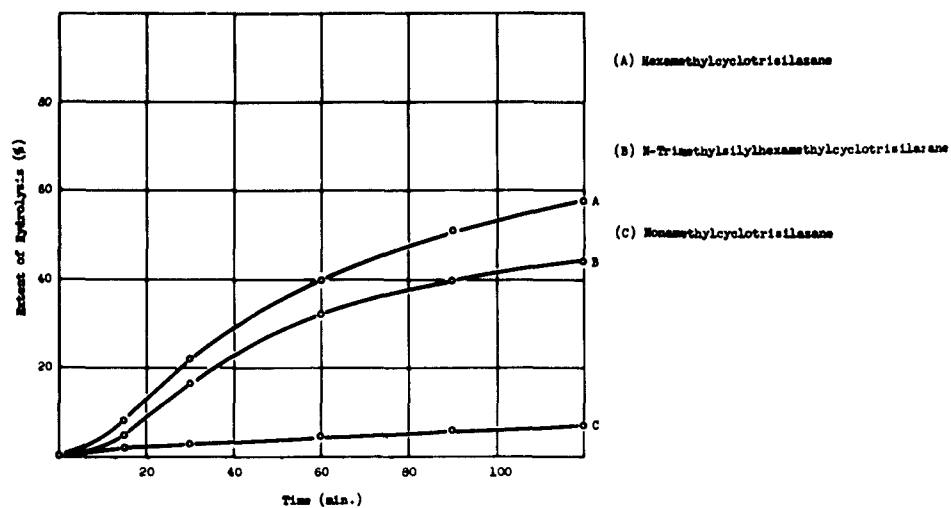


Fig. 1 - Hydrolytic Stability of Monomers

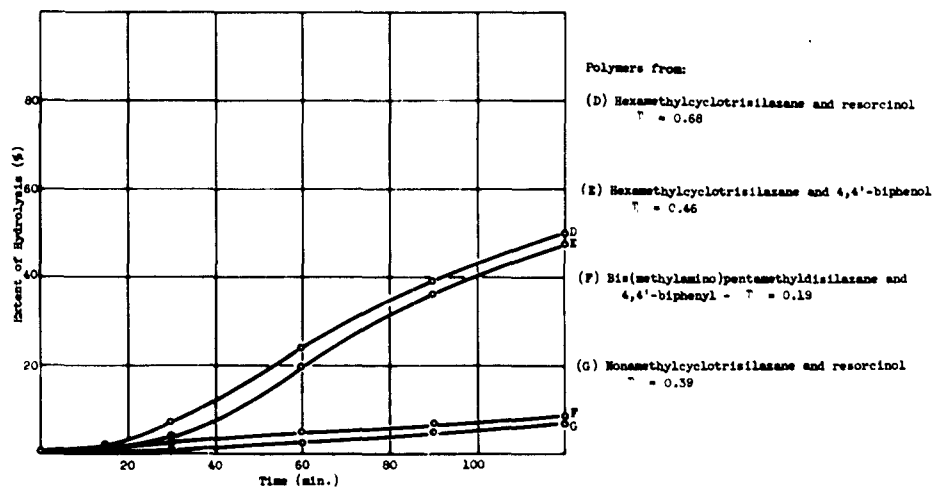


Fig. 2 - Hydrolytic Stability of Polymers

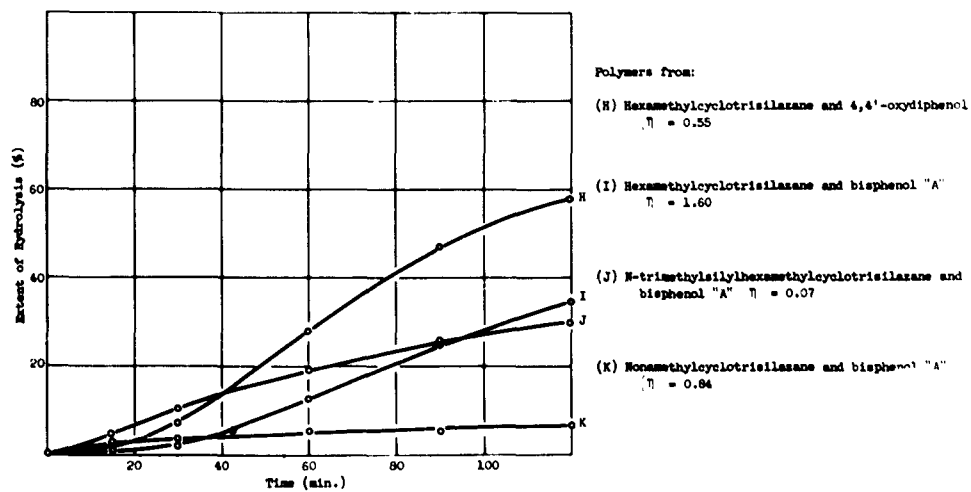


Fig. 3 - Hydrolytic Stability of Polymers

3. Polymerization in the absence of solvents: Although reasonably high degrees of polymerization have been achieved in the reaction of diols and nonamethylcyclotrisilazane, N-silylated derivatives of hexamethylcyclotrisilazane produced only materials with low intrinsic viscosities. Attempts have been made to effect polymerization in absence of solvents in order that higher temperatures can be used to assist building a polymer chain. Several of these experiments have been carried out with systems containing hexamethylcyclotrisilazane, but conditions have not yet been found that give polymers equaling those obtained in solvents. The results are summarized in the experimental section.

B. Reactions of Cyclic Silazanes Under the Influence of Acids and Bases

An investigation of possible rearrangement reactions of cyclic silazanes to linear materials under the influence of acidic and basic catalysts was initiated in the last report period and summarized in the last Quarterly Progress Report. In a continuation of this work, octamethylcyclotetrasilazane, heated in the presence of titanium tetrachloride, antimony pentachloride, or ammonium bromide at 175°, gave mixtures containing the trimer, tetramer, and undistillable residues. No significant reactions were observed with ammonium chloride or stannic chloride.

It is apparent that in the presence of acids at 175° a randomization of the silazane system occurs, and that both the trimer and tetramer can be expected as products. Speculation on the nature of the undistillable residues is unjustified because of the great probability that silicon-carbon cleavage can occur under the experimental conditions.

C. Silicon-Nitrogen Polymer Containing Phenylene Groups

Monomers with the following structures were prepared for use in polymerization reactions.



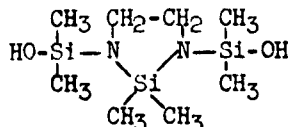
Compounds in which R equals methyl and n-butyl were prepared and characterized, but the generally low yield indicated that significant side reactions took place in the condensation of the amines with the required chlorosilane. Attempts to prepare the amino derivative gave nonvolatile residues.

p-Phenylenebis(dimethylmethylaminosilane), heated in xylene in the presence of ammonium sulfate, gave a tough, slightly elastic polymer with an intrinsic viscosity of 0.19. This polymer will be examined for its hydrolytic stability.

D. Other Experiments

Recent publications²⁻⁴ have indicated that good yields of hexamethyldisilazane can be obtained by the ammonolysis of chlorodimethylsilane in concentrated liquid ammonia solutions of ammonium nitrate (Diver's solutions). It was of considerable interest to determine the fate of the difunctional dichlorodimethylsilane under these extreme conditions. With this procedure, dichlorodimethylsilane gave a mixture of hexamethylcyclotrisilazane, octamethylcyclotetrasilazane, and a nonvolatile residue, none of the components being obtained in a particularly good yield. The method, therefore, does not appear particularly useful as a method of preparing either monomeric materials or polymers.

Another potentially useful monomer is the partial hydrolysis product of 1,3-bis(dimethylmethylaminosilyl)-2,2-dimethyl-1,3-diaza-2-silacyclopentane.



Controlled hydrolysis of the aminosilane gave a product that polymerized spontaneously at room temperature to a brittle infusible polymer. Because of the lack of stability of the monomer and the apparent crosslinking that occurs during its polymerization, the study of this monomer has been abandoned.

III. FUTURE WORK

It is anticipated that work during the next quarter will emphasize the following:

1. Additional screening of monomers and polymers for the selection of the most hydrolytically and thermally stable materials.
2. The synthesis of silazane monomers likely to impart enhanced hydrolytic stability in the finished polymers prepared from organic diols.
3. The selection of polymerization methods that can increase the molecular weight of the products from the condensation of organic diols with N-substituted derivatives of cyclosilazanes.

EXPERIMENTAL PART

A. Hydrolytic Stability of Silicon-Nitrogen Compounds and Polymers

In a series of preliminary experiments, a solution of a silazane or silazane polymer (0.1 to 0.2 g.), dissolved in 20 ml. of solvent, was hydrolyzed at constant temperature. Nitrogen was passed through the system at a rate of about 60 ml/min and the effluent gases were bubbled through a 2 per cent boric acid solution. At zero time, the measured quantity of water was added to the hydrolysis flask, and the extent of hydrolysis at various time intervals was determined by titrating the boric acid solution with 0.01 N hydrochloric acid using a mixture of bromcresol green and methyl red as an indicator. Experimental conditions and results are summarized in Table I.

The following is a typical example of a hydrolysis experiment employing the conditions found in the preliminary runs to be most advantageous. The results of a series of experiments in which these conditions are employed are given in Table II and Figs. 1, 2, and 3.

A solution of 0.0997 g. (0.000455 mole) of hexamethylcyclotrisilazane in 10 ml. of toluene (dried over calcium chloride) was introduced into a 100 ml. thermowell flask equipped with a 12 in. condenser. After the mixture was heated to 65°, 20 ml. of a 2.5 per cent solution of water in methanol was added from the top of the condenser (zero time). Nitrogen was introduced through a tube extending through the condenser to the bottom of the flask, and effluent gases were passed through 20 ml. of a freshly prepared 2 per cent boric acid solution. A nitrogen flow of 30 ml/min and a temperature of 65° was maintained throughout the run. At intervals of 15, 30, 60, 90, and 120 min. the boric acid-containing traps were replaced and the ammonia evolved during each time period, titrated with a 0.01 N hydrochloric acid using a bromcresol green and methyl red mixed indicator. The extent of hydrolysis was calculated from the amount of ammonia collected in each trap.

The data and results of this run and runs with silazane polymers are shown in Table III.

TABLE I

PRELIMINARY HYDROLYSIS STUDIES

<u>Solvent</u>	<u>Water (ml.)</u>	<u>Temp. (°C)</u>	<u>Extent of Hydrolysis (% in min.)</u>
<u>Hexamethylcyclotrisilazane</u>			
1,4-Dioxane	0.5	30	79.5 in 102 min., 96.4 in 223.3 min.
N,N-Dimethylformamide	0.5	30	64.5 in 120 min.
Toluene	0.5 in methanol ^{a/}	64	57.8 in 120 min.
<u>N-(Trimethylsilyl)hexamethyl- cyclotrisilazane</u>			
1,4-Dioxane	0.5	30	14.4 in 120 min.
<u>Polymer^{b/}</u>			
1,4-Dioxane	0.5	30	12.4 in 120 min., 19.4 in 210 min.
Acetone	0.5	30	21.1 in 90 min.
N,N-Dimethylformamide	0.5	30	64.5 in 120 min.
Diethyleneglycol dimethyl- ether	0.5	30	44.9 in 120 min.
Diethyleneglycol dimethyl- ether ^{c/}	0.5	30	10.4 in 120 min.
Diethyleneglycol dimethyl- ether ^{c/}	1.0	40	12.9 in 120 min.
Diethyleneglycol dimethyl- ether ^{c/}	0.5	50	21.8 in 120 min.
1,4-Dioxane ^{c/}	0.5	50	2.7 in 60 min.

TABLE I (Concluded)

<u>Solvent</u>	<u>Water (ml.)</u>	<u>Temp. (°C)</u>	<u>Extent of Hydrolysis (% in min.)</u>
<u>N,N</u> -Dimethylformamide	0.5 ^d /	50	38.6 in 90 min.
Toluene ^c /	2.0 in DMF ^a /	40	37.9 in 120 min., 58.7 in 180 min.
Toluene ^c /	0.5 in methanol ^a /	63	55.8 in 120 min.
Benzene	0.5 in methanol ^a /	60	45.6 in 120 min.

a/ Water added as a solution in 20 ml. solvent at zero time.

b/ Polymer from hexamethylcyclotrisilazane and 4,4'-oxydiphenol.

c/ Dried over calcium chloride.

d/ Water added after 45 min. when 14.5 per cent of the ammonia had distilled out.

TABLE II
HYDROLYTIC STABILITY OF SILAZANES AND SILAZANE POLYMERS

<u>Silazane or Polymer</u>	<u>Extent of Hydrolysis</u>	
	<u>Time (min.)</u>	<u>%</u>
Hexamethylcyclotrisilazane	15	7.5
	30	21.1
	60	39.7
	90	50.5
	120	57.6
N-(Trimethylsilyl)hexamethylcyclotrisilazane	15	4.9
	30	16.6
	60	32.0
	90	39.9
	120	44.2
Nonamethylcyclotrisilazane	15	2.1
	30	3.0
	60	4.6
	90	6.0
	120	7.1
Polymer from Hexamethylcyclotrisilazane and 4,4'-Oxydiphenol	15	2.3
	30	7.3
	60	27.8
	90	46.5
	120	58.0
Polymer from 1,3-Bis(methylamino)pentamethyldisilazane and 4,4'-Dihydroxybiphenyl	15	1.6
	30	2.3
	60	4.8
	90	6.8
	120	8.4
Polymer from Hexamethylcyclotrisilazane and 4,4'-Dihydroxybiphenyl	15	0.3
	30	3.5
	60	19.8
	90	36.1
	120	47.5
Polymer from N-(Trimethylsilyl)hexamethylcyclotrisilazane and Bisphenol "A"	15	4.4
	30	10.0
	60	19.2
	90	25.6
	120	30.0
Polymer from Hexamethylcyclotrisilazane and Bisphenol "A"	15	0.5
	30	1.9
	60	12.6
	90	24.8
	120	34.6
Polymer from Nonamethylcyclotrisilazane and Bisphenol "A"	15	2.5
	30	3.2
	60	5.1
	90	6.0
	120	6.7
Polymer from Nonamethylcyclotrisilazane and Resorcinol	15	0.09
	30	0.45
	60	2.5
	90	5.0
	120	7.0
Polymer from Hexamethylcyclotrisilazane and Resorcinol	15	1.2
	30	6.9
	60	24.0
	90	39.0
	120	50.0

TABLE III

POLYMERS FROM SILAZANES AND ORGANIC DIOLS

<u>Diol^{a/}</u>	<u>Solvent</u>	<u>Polymerization Temp. and Time (°C/hr)</u>	<u>Amine Evolved (%)</u>	<u>Polymer Yield (%)</u>	<u>[η] (toluene)</u>	<u>Polymer Description</u>
<u>Hexamethylcyclotrisilazane with:</u>						
Bisphenol "A" ^{b/}	Xylene	200-210°/5 hr	74.5	-	0.90	Clear gum
Bisphenol "A" ^{c,d/}	Toluene	114°/24 hr	-	92.4	0.83	Elastic gum
Bisphenol "A" ^{e,f/}	Toluene	115°/12 hr	69.2	90.5	0.63	Soft, tacky rubbery solid
Bisphenol "A" ^{g/}	Toluene	110-130°/24 hr	89.4	95.2	1.26	Rubbery, elastic solid
2,2,4,4-Tetramethyl-1,3-cyclobutanediol ^{h/}	Toluene	118-155°/70 hr	81.0	92.2	0.26	Viscous, tacky liquid
2,2,4,4-Tetramethyl-1,3-cyclobutanediol	Xylene	151-165°/62 hr	87.2	90.8	0.25	Viscous, tacky liquid
4,4'-Oxydiphenol ^{h/}	Toluene	117°/24 hr	86.5	100.0	0.55	Elastic gum
4,4'-Bis(hydroxymethyldiphenyl ether	Xylene	160°/24 hr	84.8	82.2	0.61	Elastic gum
4,4'-Bis(hydroxymethyl)-diphenyl ether	Toluene	115-19°/48 hr	64.1	86.0	0.10	Rubbery gum
4,4'-Bis(hydroxymethyl)-diphenyl ether	Pyridine	120°/24 hr	84.0	95.0	0.165	Soft, tacky gum
4,4'-Bis(hydroxymethyl)-diphenyl ether	Xylene	145°/24 hr	78.0	90.0	0.14	Soft, tacky gum
4,4'-Dihydroxybiphenyl ^{i/}	Toluene	115°/24 hr	85.0	Quant.	0.46	Rubbery solid
<u>Nonamethylcyclotrisilazane with:</u>						
Bisphenol "A"	Toluene	118°/24 hr	86.4	81.5	0.84	Tough, elastic solid
Bisphenol "A" ^{e/}	Toluene	115°/24 hr	86.4	83.0	0.33	Soft, rubbery solid
<u>Bis(methylamino)pentamethyldisilazane with:</u>						
Bisphenol "A" ^{e/}	Toluene	130°/24 hr	84.5	89.4	0.76	Tough, rubbery solid
4,4'-Dihydroxybiphenyl ^{e/}	Toluene	112°/24 hr	75.3	94.0	0.18	Glassy solid
<u>N-(trimethylsilyl)hexamethylcyclotrisilazane with:</u>						
Bisphenol "A"	Toluene	130-140°/24 hr	85.8	97.5	0.065	Tacky, viscous liquid

^{a/} Peninsular; redistilled, b.p., 111-15°, n_D^{29} 1.4408.

^{b/} Eastman; m.p., 115-16°.

^{c/} 2,4,6-Trimethyl-2,4,6-trivinylcyclotrisilazane (0.3 mole per cent) added.

^{d/} In this run, larger quantities were used and a 35 g. sample of the product was forwarded to Rock Island Arsenal for testing.

^{e/} 2,4,6-Trimethyl-2,4,6-trivinylcyclotrisilazane (3.0 mole per cent) added.

^{f/} Sixty milliliters of toluene was used as a solvent, and the mixture was stirred throughout the polymerization.

^{g/} Eastman; m.p., 125-35°.

^{h/} Eastman; m.p., 166-7°.

^{i/} Dow; recrystallized three times from toluene and once from isopropyl alcohol, m.p., 133-4°.

^{j/} Eastman; m.p., 276-8°.

B. Polymers from Silazanes with Organic Diols

Procedures similar to those described in Quarterly Progress Report No. 5, page 8 were followed for new experiments in this series. The results are summarized in Table III. Detailed observations on one larger scale run are given in the following section.

1. Hexamethylcyclotrisilazane-bisphenol "A" polymer - sample preparation for curing studies: A mixture of 32.2 g. (0.147 mole) of hexamethylcyclotrisilazane, 0.76 g. (0.003 mole) of 2,4,6,-trimethyl-2,4,6,-trivinylcyclotrisilazane, 34.2 g. (0.15 mole) of bisphenol "A" and 100 ml. toluene was heated to the reflux temperature of the mixture (116°) during a 1-hr. period. Considerable ebullition was observed during the initial heating period, and the mixture became homogenous at 60°. Additional toluene (100 ml.) was added to reduce the viscosity of the mixture, and heating was continued for 24 hr. When the gum was devolatilized by distilling out the toluene and heating the residue to 150°/ < 1 mm, 64.0 g. (99 per cent yield) of the polymer was obtained, $[\eta] = 1.22$. This material was forwarded to Rock Island Arsenal for crosslinking studies.

2. Melt polymerization of hexamethylcyclotrisilazane with organic diols: In a typical experiment, about 1.0 g. (0.0044 mole) of bisphenol "A" and 1.0 g. (0.0044 mole) of hexamethylcyclotrisilazane were mixed and heated in an 8 x 150 mm. test tube placed in an oil bath at 60° (T_1) for 15 min. Subsequently, the temperature of the bath was raised to 200° (T_2) over an 0.5 hr. period and heating was continued at the second temperature an additional 0.5 hr. The cooled gum-like material had an intrinsic viscosity in toluene of 0.29.

Other experiments, which followed this general procedure are summarized in Table IV.

3. Other data: Elemental analyses have been received for a hexamethylcyclotrisilazane-bisphenol "A" condensation product. The results of these analyses and those reported earlier are summarized in Table V.

Several differential thermal analysis traces obtained during this report period are summarized in Figs. 4, 5, 6, and 7.

TABLE IV

MELT POLYMERIZATION OF HEXAMETHYLCYCLOTRISILAZANE WITH ORGANIC DIOLS

Run No.	Organic Diol	T ₁ (°C/hr)	Heating Time T ₁ to T ₂ (hr.)	T ₂ (°C/hr)	[η] (Toluene)	Polymer Description
1	Bisphenol "A"	60°/0.25	0.5	200°/0.5	0.29	Gum
2	Bisphenol "A"	55°/0.25	0.5	250°/0.5	1.25	Hard elastic gum
3 ^a /	Bisphenol "A"	55°/0	0.5	250°/1.0	0.38	Gum
4 ^b /	Bisphenol "A"	45°/0	1.0	200°/5.0	0.39	Gum
5	4,4'-Bis(hydroxy- methyl)diphenyl ether	130°/0	0.5	205°/5.0	Insoluble ^c /	Gum
6 ^d /	4,4'-Bis(hydroxy- methyl)diphenyl ether	60°/0	1.0	205°/3.0	0.23	Gum

^a/ Ammonia yield, 76 per cent.

^b/ Ammonia yield, 80 per cent.

^c/ The polymer swelled in toluene, but was not completely soluble.

^d/ The monomers were mixed in 1.0 ml. xylene.

TABLE V

ELEMENTAL ANALYSES OF POLYMERS

<u>Polymer from:</u>	<u>[η] (Toluene)</u>	<u>Calcd. for:</u>	<u>Elemental Analyses</u>					
			<u>C</u>		<u>H</u>		<u>N</u>	
			<u>Calcd.</u>	<u>Found</u>	<u>Calcd.</u>	<u>Found</u>	<u>Calcd.</u>	<u>Found</u>
Hexamethylcyclotrisilazane and resorcinol	0.72	$C_{12}H_{24}N_2O_2Si_3$	46.10	47.82	7.74	7.59	8.96	8.71
							26.96	26.11
Hexamethylcyclotrisilazane and 1,4-benzenedimethanol	0.45	$C_{14}H_{28}N_2O_2Si_3$	49.36	49.62	8.28	8.22	8.23	7.83
							24.74	24.22
Hexamethylcyclotrisilazane and bisphenol "A"	1.60	$C_{21}H_{34}N_2O_2Si_3$	58.55	58.77	7.96	7.72	6.50	6.35
							19.56	19.36

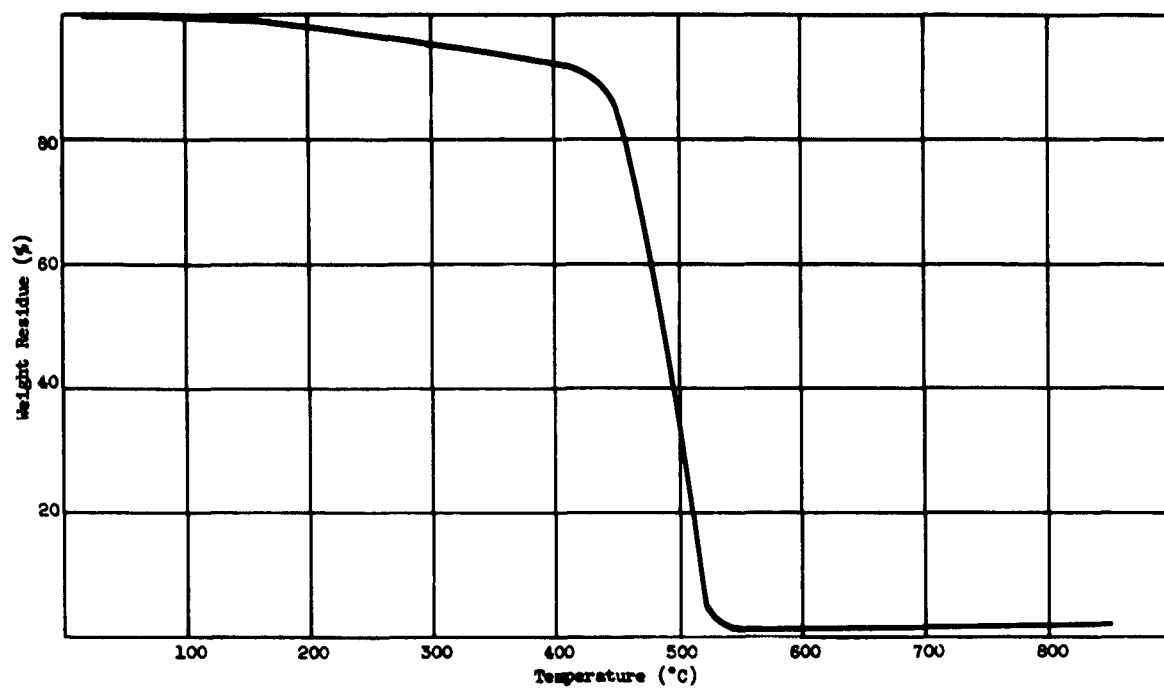


Fig. 4 - Thermogravimetric Analysis of SE 52 (General Electric Methyl Phenyl Silicone Gum) - Heating Rate 3°/min

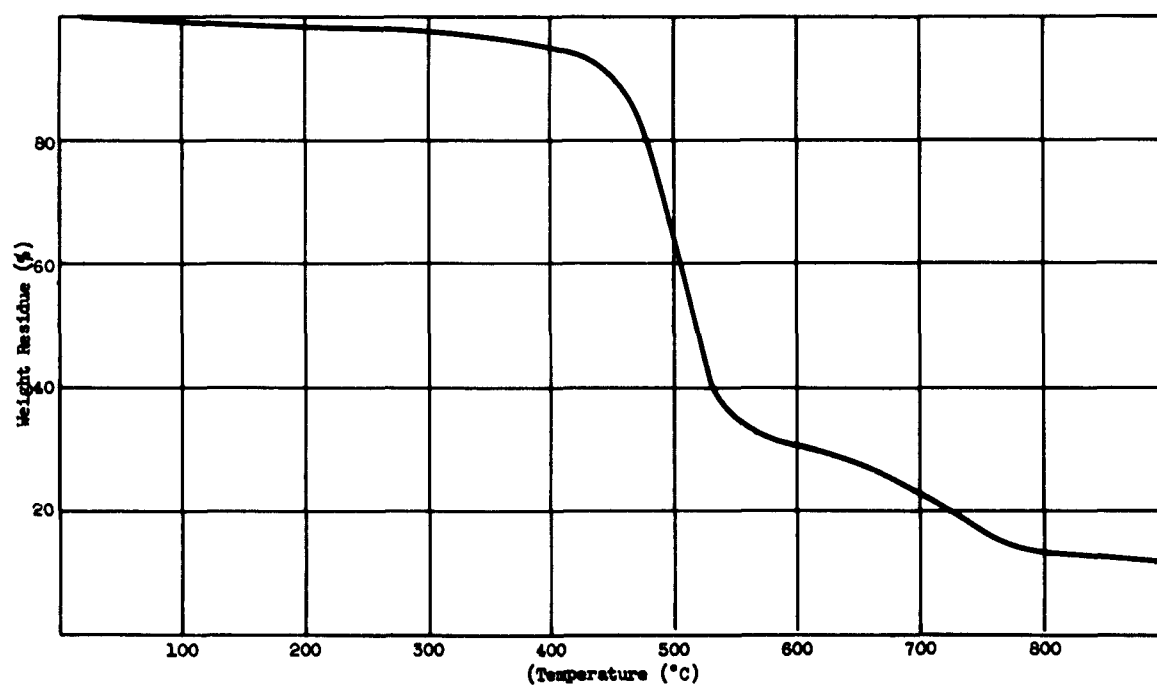


Fig. 5 - Thermogravimetric Analysis of Bis(methylamino)-pentamethyldisilazane - Bisphenol "A" Polymer - Heating Rate 3°/min

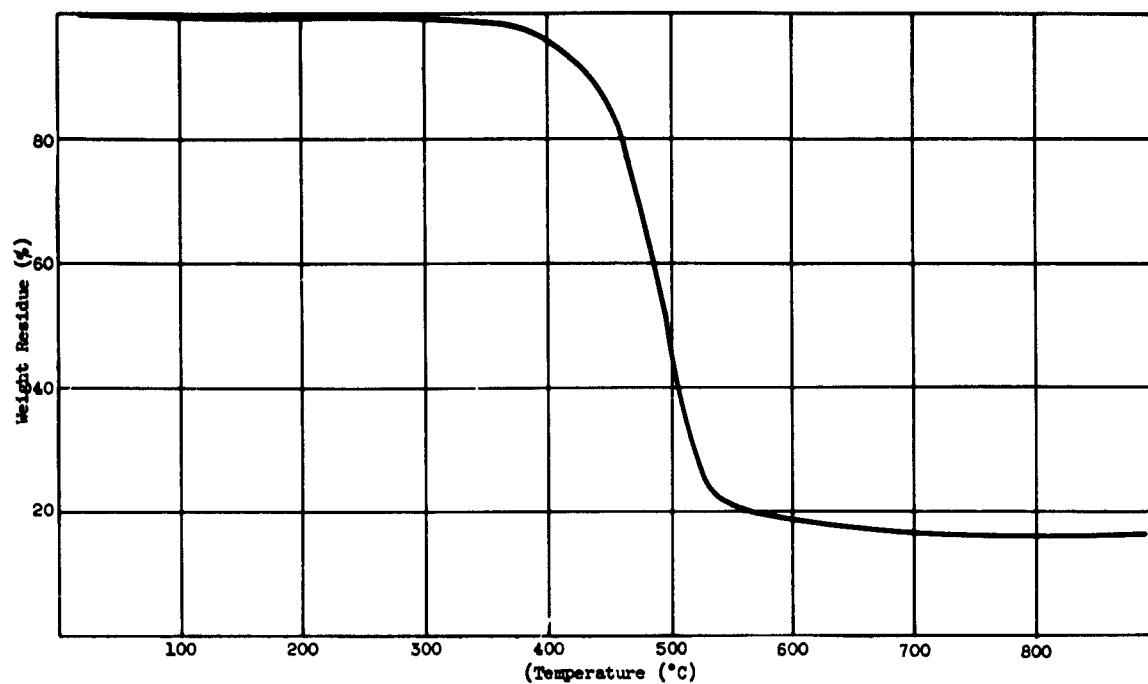


Fig. 6 - Thermogravimetric Analysis of Nonamethylcyclotrisilazane - Bisphenol "A" Polymer - Heating Rate 3°/min

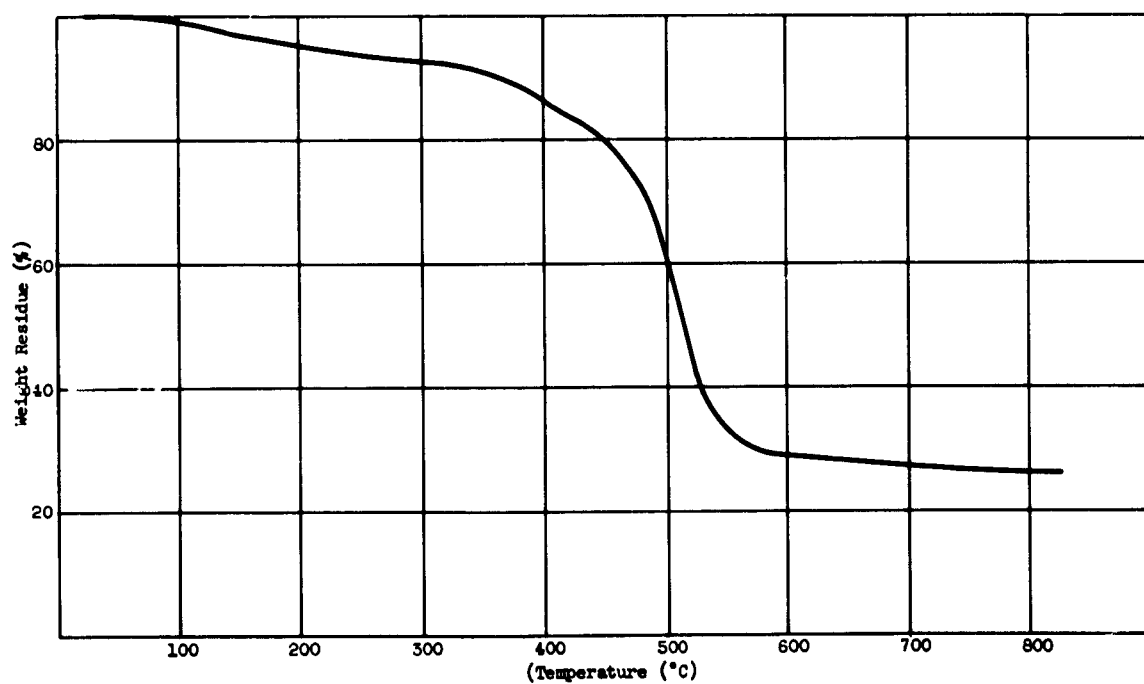


Fig. 7 - Thermogravimetric Analysis of Hexamethylcyclotrisilazane - Bisphenol "A" Polymer - Heating Rate 3°/min

C. Rearrangement Reactions of Cyclosilazanes

1. Reactions of octamethylcyclotetrasilazane with various metal halides: Octamethylcyclotetrasilazane (5.0 g.) was heated with various anhydrous metal halides (1 per cent by weight) for 4 hr. at 175°. Somewhat impure tetramer, m.p. 87-91°, was used in these experiments. The following results were obtained:

With stannic chloride: When the product was dissolved in 20 ml. of Skellysolve "B", filtered, and devolatilized under vacuum, 4.0 g. (80 per cent) of the tetramer was recovered, m.p. 82 - 9°.

With titanium tetrachloride: Filtration of a solution of the residue and distillation of the filtrate gave 1.0 g. (20 per cent yield) of hexamethylcyclotrisilazane boiling at 95 - 105°/75 mm, n_D^{29} 1.4408 (reported, n_D^{20} 1.4448). A liquid polymer, 2.4 g., at 200°/< 1 mm remained undistillable ($[\eta] = 0.043$).

With antimony pentachloride: A similar purification procedure gave 2.0 g. (40 per cent yield) of hexamethylcyclotrisilazane boiling at 73 - 85°/11 mm, n_D^{28} 1.4417. A solid residue which weighed 2.8 g. contained mostly tetramer.

With ammonium bromide: When a solution of the product was filtered and distilled, 1.6 g. (32 per cent yield) of hexamethylcyclotrisilazane boiling at 76°/11 mm., n_D^{28} 1.4408, and 0.5 g. (10 per cent) of sublimed tetramer, melting at 92 - 4° were obtained. The residue, undistillable at 200°/< 1 mm, weighed 2.7 g., $[\eta] = 0.042$ (toluene).

With ammonium chloride: When the product was dissolved in 20 ml. of Skellysolve "B", filtered, and devolatilized under vacuum, 4.5 g. (90 per cent) of the tetramer was recovered, m.p. 94 - 5°.

With aluminum bromide: Filtration of a solution of the residue and distillation of the filtrate gave 1.3 g. (26 per cent) of hexamethylcyclotrisilazane boiling at 73 - 8°/11 mm, n_D^{29} 1.4408, 1.1 g. of sublimed tetramer (a 22 per cent recovery) melting point 87 - 90°. The liquid residue, undistillable at 200°/21 mm, $[\eta] = 0.035$, weighed 2.0 g.

2. Octamethylcyclotetrasilazane and ammonium bromide: A mixture of 10.0 g. (0.034 mole) of the tetramer and 0.10 g. of ammonium bromide was heated at 175° for 4 hr. Ammonia, 10.86 meq., was collected in an acid trap and titrated. Filtration of a solution of the residue and distillation of the filtrate gave 1.5 g. (15 per cent yield) of hexamethylcyclotrisilazane boiling at 72 - 8°/11 mm, n_D^{27} 1.4410, 1.0 g. (10 per cent recovery) of sublimed tetramer, m.p., 88 - 92°, and 6.1 g. of a viscous liquid residue that was not distillable at 200°/< 1 mm, $[\eta] = 0.043$.

3. Octamethylcyclotetrasilazane and aluminum chloride: A mixture of 10.0 g. (0.0342 mole) of octamethylcyclotetrasilazane, m.p. 88 - 92°, and 0.12 g. (1.2 per cent) of anhydrous aluminum chloride was heated at 175° for 4 hr. Ammonia, 8.05 meq., was evolved and swept with nitrogen into an acid trap connected to the system. After the product was diluted with 10 ml. of Skellysolve "B" and filtered, the solvent was distilled out and the residue was fractionally distilled to give 0.7 g. (7 per cent yield) of hexamethylcyclotrisilazane, b.p. 90 - 100°/85 mm, n_D^{29} 1.4418, 1.1 g. of unchanged starting material contaminated with the trimer, b.p. near 130°/35 mm, and 4.5 g. of polymeric residue that was not distillable at 200°/1 mm, $[\eta] = 0.046$.

D. Phenylene-Linked Silazane Polymers

1. p-Phenylenebis(chlorodimethylsilane): The subject compound was prepared according to a method described in the literature⁵ and obtained a yield of 38.9 per cent, b.p. 108 - 10°/1.5 mm.

2. p-Phenylenebis(dimethylmethylaminosilane): Fifty milliliters of a toluene solution containing 8.2 g. p-phenylenebis(chlorodimethylsilane) was treated with anhydrous methylamine by passing the gas over the surface of the stirred solution until the amine began refluxing in a Dry Ice condenser connected to the reaction flask. External cooling was required during the addition to maintain the reaction temperature near 25°. Filtration gave 4.9 g. of amine salts. When the filtrate was distilled, 3.0 g. (37 per cent yield) of the product boiling at 80 - 84°/0.3 mm, n_D^{28} 1.5043 was obtained. The distillation residue weighed 3.4 g.

Anal. Calcd. for $C_{12}H_{24}N_2Si_2$: C, 57.07; H, 9.58; N, 11.10; Si, 22.25.
Found: C, 56.95; H, 9.73; N, 10.91; Si, 22.02.

3. Polymerization of p-phenylenebis(dimethylmethylaminosilane): A solution of 2.6 g. (0.0107 mole) of the subject compound in 3.0 ml. of xylene and 0.026 g. (1 weight per cent) of ammonium sulfate was heated at 137° for 24 hr. A total of 8.87 meq. of methylamine (83 per cent) was collected in an acid trap and titrated. The residue was filtered and devolatilized under vacuum to give 1.7 g. (72 per cent yield) of a tough, slightly elastic polymer, $[\eta] = 0.194$.

4. p-Phenylenebis(aminodimethylsilane) (attempted): In a procedure similar to that used for the preparation of the methylamine analogue, 2.6 g. of ammonium chloride was obtained when the reaction product was filtered. Evaporation of the solvent gave a residue which would not distill at 210° and 0.1 mm. A sample for polymerization experiments was obtained in a second run by evaporating the toluene from the filtrate under reduced pressure and centrifuging the residue to remove cloudiness from the residual oil.

5. Polymerization of p-phenylenebis(aminodimethylsilane): A solution of 4.0 g. of the undistilled monomer in 4.0 ml. of xylene and 0.04 g. (1 per cent) ammonium sulfate were heated at the boiling point of xylene (138°) for 24 hr. The polymer solution was filtered, and the solvent was distilled off at reduced pressure. The weight of liquid polymer obtained was 2.6 g., $[\eta] = 0.042$.

6. p-Phenylenebis(dimethylbutylaminosilane): After 15 g. of butylamine in 25 ml. toluene was added over a 20 min. period to 50 ml. of a stirred solution of 8.2 g. of p-phenylenebis(chlorodimethylsilane) in toluene, filtration of the product gave 5.8 g. of amine salts. Fractional distillation of the filtrate gave 0.7 g. (6 per cent yield) of the subject compound boiling at 118 - 20°/0.07 mm, $n_D^{28} 1.4912$.

Anal. Calcd. for $C_{18}H_{36}N_2Si_2$: C, 64.21; H, 10.78; N, 8.32; Si, 16.69. Found: C, 63.91; H, 10.59; N, 8.15; Si, 16.52.

E. Miscellaneous Experiments

1. Ammonolysis of dichlorodimethylsilane in "Diver's solution": Anhydrous ammonia was introduced into a flask immersed in an ice bath and containing 160 g. of ammonium nitrate until all the ammonium nitrate had dissolved. The weight of the solution indicated that 56 g. of ammonia had been absorbed. To the cooled, stirred mixture was added 39 g. (0.3 mole) dichlorodimethylsilane over a 30 min. period. During the addition a copious salt precipitate formed that did not dissolve when more ammonia was introduced into the flask. The product was treated with 200 ml. anhydrous ether, stirred several minutes, and the ether layer was decanted. A second extraction was carried out with 50 ml. of ether. The ether washings were combined, the ether was distilled off, and the residue was fractionally distilled to yield 5.4 g. (25 per cent yield) of hexamethylcyclotrisilazane, boiling at 110 - 12°/85 mm, 2.0 g. of an intermediate fraction, and 2.5 g. (11 per cent yield) of octamethylcyclotetrasilazane, boiling at 130 - 45°/35 mm. The distillation residue weighed 6.6 g. and crystallized on standing.

2. 1,3-Bis(hydroxydimethylsilyl)-2,2-dimethyl-1,3-diaza-2-silacyclopentane (attempted): A stirred solution of 10 g. (0.035 mole) of freshly distilled 1,3-bis(dimethylmethylaminosilyl)-2,2-dimethyl-1,3-diaza-2-silacyclopentane, b.p. 78 - 80°/0.15 mm, in 50 ml. of diethyl ether was treated with a solution of 1.25 g. (0.016 mole) water in 100 ml. ether. The addition required 30 min. After the product was refluxed 1 hr. and 50 ml. of the ether had distilled out, the remainder of the ether was removed at reduced pressure, the temperature of the residue being kept below 20° during the evaporation.

Crystallization could not be induced when the residue was dissolved in 20 ml. of Skellysolve "F" and cooled in an acetone-Dry Ice bath. Evaporation of the petroleum ether left a mobile liquid that polymerized to a brittle gel on standing overnight. This polymer did not melt at 250°.

3. Hexamethylcyclotrisilazane and octamethylcyclotetrasilazane: Using the procedure described in the Quarterly Report No. 4, page 9, there was obtained 92.5 g. (32.6 per cent yield) of the trimer, b.p. 115 - 6°/86 mm, n_D^{27} 1.4413 and 93.1 g. (32.9 per cent yield) of the tetramer as a white solid residue.

4. N-Trimethylsilylhexamethylcyclotrisilazane: A procedure identical to that described in the Quarterly Report No. 4, page 12, was used to prepare 15.9 g. (55 per cent yield) of the subject compound, b.p. 112-13°/10 mm, n_D^{27} 1.4598.

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5. M. Sveda, U. S. Patent 2,562,000, 1951. See W. Sorenson and T. Campbell, "Preparative Methods of Polymer Chemistry," Interscience, New York, 1961, p. 131.

APPENDIX

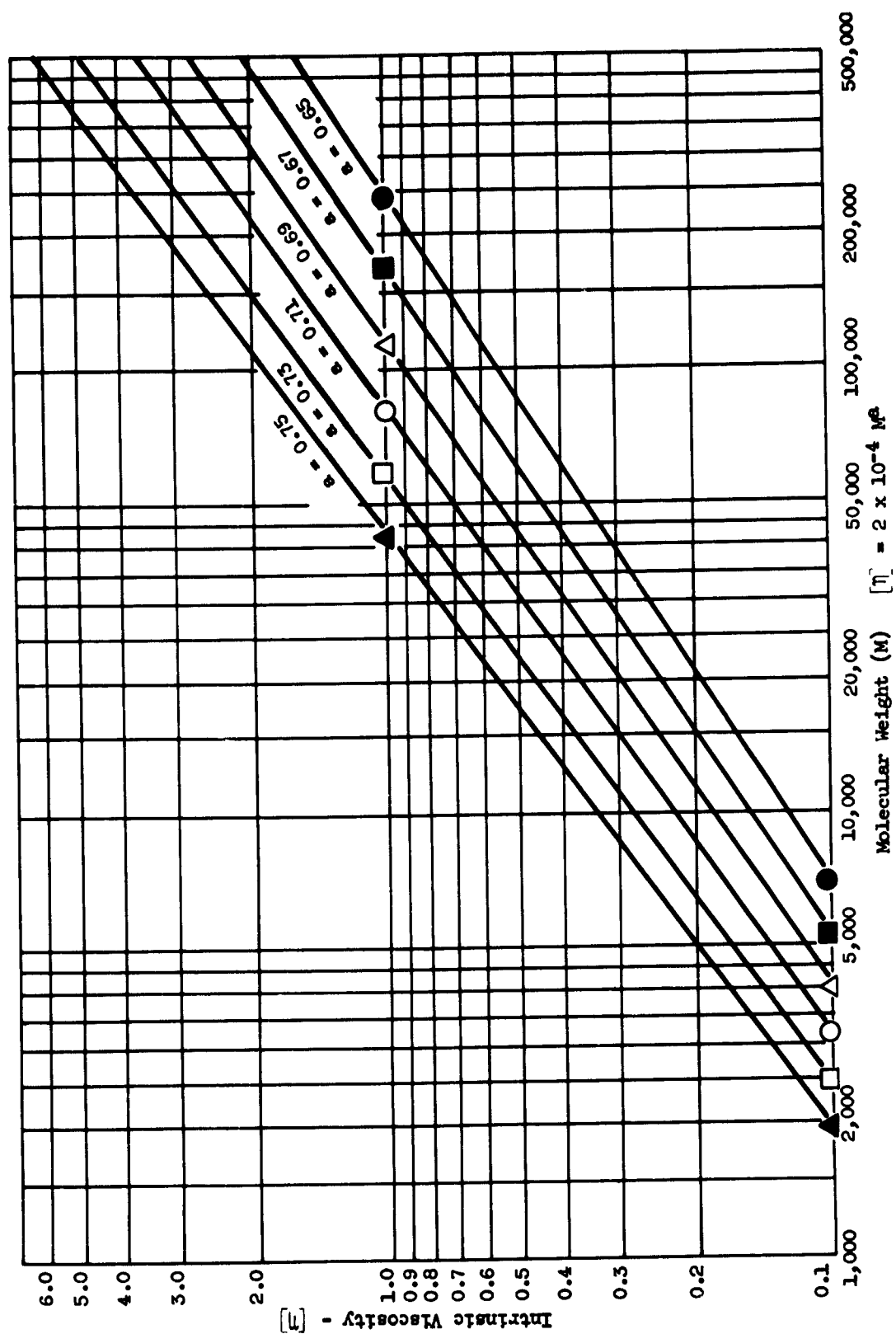


Fig. 8 - Nomograph of the Intrinsic Viscosity Versus Molecular Weight